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## STEAM ELECTROLYSIS

The present invention relates to hydrogen production, and more particularly to hydrogen production by high temperature steam electrolysis with improved efficiency and reduced cost.

Hydrogen is becoming an increasingly important fuel. Various processes have been developed for producing it including inter alia, steam reforming of natural gas and by coal gasification, and water electrolysis. Existing processes do, however, suffer from various disadvantages including relatively low efficiency and high production costs.

It is an object of the present invention to avoid or minimize one or more of the above-mentioned disadvantages.

It has now been found that by using a proton conducting electrolyte membrane, which is substantially non-permeable to oxide ions and to molecular gas, and is stable at high temperatures, it is possible to dissociate water into hydrogen and oxygen and at the same time separate the hydrogen from the oxygen.

Thus in one aspect the present invention provides a method of producing hydrogen comprising: providing a steam feed stream, contacting said steam feed stream with a proton conducting membrane supported on a porous redox stable substrate, through said substrate, said membrane being substantially non-permeable to molecular gas and to oxide ions, applying a DC voltage across an anode coupled to the substrate side of said membrane and a cathode coupled to the

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other side of said membrane so as to dissociate at least part of said steam feed stream therebetween, into protonic hydrogen and oxygen at said anode, allowing said protonic hydrogen to pass through said membrane and form molecular hydrogen at said cathode, and collecting said molecular hydrogen.

In another aspect the present invention provides a steam electrolyser for producing hydrogen, comprising: a dense proton-conducting membrane substantially non-porous to molecular gas, said membrane being supported on a gas permeable, chemically and mechanically stable, electronically conducting substrate, said membrane being coupled: at the substrate - supported side to an anode for connection to a positive voltage, and to a steam inlet and oxygen outlet for feeding a steam feed stream into said substrate and exhausting oxygen gas released therefrom; and at its other side to a cathode for connection to a negative voltage and a hydrogen gas outlet for exhaustion of hydrogen gas released at said cathode.

It should be noted that in the simplest case the anode may simply form part of the substrate adjoining the membrane where a suitable substrate is employed i.e. where the substrate material is electrochemically active.

Alternatively the anode may comprise a thin layer of a different material interposed between the membrane and the substrate support.

With the present invention the hydrogen production process is substantially simplified, whilst having a relatively high efficiency, and uses apparatus of relatively economic

construction. The process provides hydrogen gas which is free from oxygen, steam and other gases, thereby avoiding the need for any downstream separation of gases. Also the electrolysis and separation out of hydrogen gas, may be  
5 achieved without the need for any expensive precious metal catalysts or the like.

Various proton-conducting materials are known in the art which are stable to a greater or lesser extent at high  
10 temperatures. In general steam electrolysis is carried out at temperatures of around 900 to 1000 °C. A particular advantage of the present invention is, however, that steam electrolysis can be carried out at significantly lower temperatures, for example, from 500 to 700 °C, whereby the  
15 materials and construction used may be significantly simplified and reduced in cost. In general suitable proton-conducting materials comprise a material which allows the reversible dissociation of water into its lattice to form mobile protonic carriers therein. Such materials are  
20 frequently oxygen deficient perovskites of formula  $ABO_{3-\delta}$  wherein A and B represent metallic elements occupying the A and B sites of the perovskite lattice structure and  $\delta$  represents the degree of oxygen deficiency.

25 Particular preferred materials which may be mentioned include " $BaCe_{0.9}Y_{0.1}O_{2.95}$  (BCY10),  $BaZr_{0.9}Y_{0.1}O_{2.95}$  (BZY) and members of the solid solution,  $BaCe_{0.9-x}Zr_xY_{0.1}O_{2.95}$  (BCZY), or the analogues of the previously mentioned phases with lanthanides such as Gd, Nd or Yb instead of Y and such  
30 phases with higher degrees of substitution such as  $BaCe_{0.8}Y_{0.2}O_{2.95}$  (BCY20),  $Sr_3CaZr_{0.5}Ta_{1.5}O_{8.75}$  (SCZTO) and

$\text{Ba}_3\text{Ca}_{1.18}\text{Nb}_{1.82}\text{O}_{8.73}$  (BCN18) as well as composites of such materials. Thus, for example, there may be used a membrane comprising a layer of BCY10 which has relatively high electrochemical performance (in terms of proton conduction) in contact with the substrate on the hydrogen side, with an outer protective layer of SCZTO which has better stability - especially against chemical degradation by atmosphere  $\text{CO}_2$ . Similarly on an oxidising-side supported electrolyte the  $\text{BaCe}_{0.9}\text{Y}_{0.1}\text{O}_{2.95}$  (BYC10) may be protected from the high steam atmosphere by a layer of a material such as SCZTO or BZY.

As indicated above, it is also important that the membrane should be substantially impermeable to molecular gas. Accordingly the membrane material needs to be in a substantially dense, non-porous, form. The membrane is also substantially impermeable to oxide ions.

In order to maximize the efficiency of the electrolyser, the resistivity of the membrane should be kept as low as possible. Desirably therefore the membrane should be as thin as is reasonably practicable. Preferably the membrane thickness is not more than 25  $\mu\text{m}$ , advantageously from 1 to 25  $\mu\text{m}$ , most preferably from 3 to 15  $\mu\text{m}$ .

It is also important that the membrane should remain stably attached to the substrate support under the high temperature operating conditions of the electrolyser. Various methods are known in the art for forming thin films on substrates including inter alia: sol-gel techniques in which a liquid suspension is applied to a substrate, dried and then cured; tape casting in which the membrane material is provided in a powder form embedded inside a polymer tape which is placed

on the surface of the substrate and heat treated to form a substantially continuous film of membrane material; vacuum deposition in which the membrane material is provided in a powder form suspended in a liquid carrier is placed on the surface of the substrate and drawn into the surface thereof by means of a vacuum applied to the remote side of the porous substrate, and then heat treated to form a substantially continuous film of membrane material at the substrate surface; etc. It will be appreciated in relation to such processes that, in accordance with normal practice, the particle size of the membrane material applied to the surface of the porous substrate should not be significantly less than the pore size of the substrate, in order to minimize penetration of the particles into the interior of the substrate. Using such techniques we have successfully obtained proton conducting ( $\text{Sr}_3\text{CaZr}_{0.5}\text{Ta}_{1.5}\text{O}_{8.75}$ ) membrane films on porous conductive substrates (Ni:YSZ and LSM,  $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ ) with film thicknesses in the range from 3 to 100 microns, depending on the number of layers deposited.

Membranes of  $\text{BaZrO}_3$ -based materials are especially preferred as these are stable and exhibit high proton conductivity. Those materials have, though, to be sintered at a temperature above  $1600^\circ\text{C}$  which makes it very difficult to find suitable electrode materials which have so high a melting point without undergoing significant chemical reactions with the  $\text{BaZrO}_3$ -based electrolyte. By using a sintering aid such as  $\text{ZnO}$ , it is, however, possible to reduce substantially the sintering temperature, whilst still obtaining a high density product and substantially maintaining the desirable properties of high proton conductivity and stability. More particularly we have found

that by using a relatively small amount of ZnO - typically around 1% w/w, it is possible to reduce the sintering temperature of  $\text{BaZr}_{1-x}\text{Y}_x\text{O}_{3-x/2}$  from around 1700°C to around 1300°C, albeit desirably a sintering temperature of at least 1350°C should normally be used, and obtain a high density material with a relative density of the order of 96%.

In general suitable sintering aids comprise  $\text{Al}_2\text{O}_3$ ,  $\text{Bi}_2\text{O}_3$  and some first row transition elements oxides such as  $\text{TiO}_2$ ,  $\text{Fe}_2\text{O}_3$ , CoO, CuO etc, which are commonly used as sintering aids for obtaining dense ionic conducting materials such as yttria stabilised zirconia (YSZ) and ceria doped with gadolinia (CGO).

In order to have a significant effect in reducing the sintering temperature, it is generally necessary to use a minimum amount of the sintering aid. This can be readily determined by trial and error and is typically of the order of from 0.1 to 0.5 %w/w. In order to avoid significant distortion of the membrane material structure and adverse effects on the proton-conducting and stability properties thereof, it is generally desirable that the amount of sintering aid should be minimized - whilst still maintaining a useful sintering temperature reduction. Desirably there should be used not more than 5 %w/w, preferably not more than 2 %w/w, of sintering aid.

The sintering mechanism is typically due to the formation of low melting phases between the sintering aid and constituent oxides, which lower the sintering temperature. Alternatively the sintering aid enters the oxide lattice and produces a lower melting phase that sinters more readily. In either

mechanism the sintering aid may be lost on sintering. Without in any way wishing to restrict the scope of the present invention, it is believed that in this case it seems that the sintering aid acts as a dopant that essentially  
5 replaces some of the B-site ions and the solid solution  $\text{BaZr}_{1-x-z}\text{Y}_x\text{M}_z\text{O}_{3-z-x/2}$  forms wherein M represents a dopant metal and Z represents the level of B-site ion replacement and is typically in the range from 0.05 to 0.25, preferably at least 0.1. Suitable dopants include one or more oxides of  
10 M = Al, Ti, Bi, B, Mn, Mg, Zn, Co, Ni, Fe, Cu, especially Zn. The mentioned elements may be added into the materials in the form of oxide, carbonate, nitrate, chloride, carbide, nitride, etc and, through any method such as solid state reaction, sol-gel process or any form and technology known  
15 as the art. It will be appreciated that some sintering aids are more effective than others and that some sintering aids will require higher concentrations thereof. In this connection Zn doped oxides are particularly good low temperature sintering aids. Preferably substantially pure  
20 ZnO is used. In general the amount of dopant used may be from 0.1 to 5 % w/w, preferably 0.5 to 3% w/w. In the case of ZnO there is conveniently used about 1% w/w of the ZnO.

The use of such sintering aids is similarly beneficial with  
25 other membrane material such as Barium Yttrium Cerate and especially Barium Yttrium Cerate Zirconate which combines stability and conductivity performance.

Various porous electrically conducting materials which are  
30 stable at the elevated temperatures used in steam electrolyzers are already known in the art, and may be used for the substrate support in the present invention.

Suitable materials generally comprise a metallised ceramic or a mixed conductive oxide having an electrical conductivity of not less than  $10 \text{ Scm}^{-1}$ , preferably not less than  $100 \text{ Scm}^{-1}$ , at the operating temperature of the steam electrolysis. Particular suitable substrate materials which may be mentioned include metallised ceramics such as  $\text{Cu:Al}_2\text{O}_3$  or mixed conductive oxides such as  $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$  (LSM), chromium-doped LSM (i.e.  $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_3$ ) or  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-d}$  (LSCF).

10

As indicated above, the substrate support requires generally to be sufficiently porous to facilitate penetration of the steam molecules to the membrane and to facilitate exhaustion of oxygen molecules exiting from the membrane. In general therefore the pore size should be not less than  $0.5 \mu\text{m}$ , and conveniently from  $0.5$  to  $10 \mu\text{m}$ . Desirably the porosity is from 30 to 60 %, preferably from 40 to 50%. Where such a discrete anode is provided between the membrane and the substrate, it will be appreciated that in such cases the membrane is supported indirectly by the substrate.

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Generally in such cases the anode layer is deposited on the substrate, and then the membrane layer deposited onto the anode layer. Various techniques are known in the art, including those described elsewhere herein, for producing thin film layers onto substrates of various kinds.

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As noted above, a thin layer (generally  $10$  to  $100 \mu\text{m}$ , preferably  $30$  to  $50 \mu\text{m}$ ) of the substrate support itself may conveniently function as the anode of the electrolytic apparatus, (where the substrate material is electrochemically active), and is connected to the voltage

30



supply via a porous metal current collector in generally known manner. A porous cathode requires generally to be sufficiently porous to facilitate exit of hydrogen molecules from the membrane. In general therefore the pore size  
5 should be not less than 0.5  $\mu\text{m}$ , and conveniently from 0.5 to 10  $\mu\text{m}$ . Desirably the porosity is from 30 to 60 %, preferably from 40 to 50%. The cathode may be provided on the surface of the membrane electrolyte by painting, screen printing or sol-gel coating, and is connected to the voltage  
10 supply via a porous metal current collector in generally known manner. Suitable cathodes are conveniently of a transition metal such as porous metallic platinum or palladium, or a Ni cermet of a transition metal and a proton conducting electrolyte. Various mixed conducting oxides  
15 which may also be used, are known in the art including perovskite oxide materials such as those disclosed in WO2004/013925.

One of the benefits of the invention is that the lower  
20 working temperatures allow the use of less expensive current collector metals such as steel, which may, if desired, be provided with electrically conducting protective film coatings, e.g. of chromium.  
(as well as avoiding the use of expensive precious metal  
25 catalysts etc).

The substrate supported membrane, electrode, and current collector, assembly may be electrically insulated from the gas supply and exhaust pipes and any external housing, which  
30 are generally made of metal e.g. steel, by means of a high

temperature glass ceramic such as barium silicate or a high temperature cement.

As indicated above the steam electrolysis may be carried out  
5 at a range of different temperatures. It will also be understood that higher temperatures have the advantage of reducing the direct electrical energy input required. It is, however, a key feature of the present invention that it allows the use of lower temperatures than have been used  
10 heretofore in steam electrolysis, which in turn allows the use of significantly more economic materials and forms of construction. It is also important to avoid using higher temperatures as these can result in oxide ion conductivity developing in the membrane and even permeability to water  
15 molecules. Preferably there is used an operating temperature of from 400 to 800 °C, most preferably from 500 to 700 °C.

In general it is convenient to use a steam supply at a  
20 temperature substantially equal to the desired operating temperature at the membrane. It is also possible though to supply steam at a lower temperature and to heat the substrate supported membrane, e.g. using an external electrical or fuel gas (conveniently hydrogen), furnace.

25

It will also be understood that the voltage required to be applied across the membrane for a given hydrogen flux will depend on the electrical resistance of the membrane, and any supporting substrate employed. The electrical resistance  
30 will in turn depend on the particular materials used, as well as the thickness thereof, and the operating temperature used. It is accordingly desirable that the membrane should

be as thin as is reasonably practicable i.e. whilst still maintaining gas tightness and structural integrity under the operating conditions used. Typically we have found that useful levels/rates of electrolysis may be obtained with an  
5 applied voltage of the order of 1.1 to 1.2 V when using a proton conducting ( $\text{BaCe}_{0.9}\text{Y}_{0.1}\text{O}_{2.95}$ ,  $\text{Ba}_3\text{Ca}_{1.18}\text{Nb}_{1.82}\text{O}_{8.73}$ , etc) membrane having a thickness of around 25  $\mu\text{m}$ .

The feed stream may be supplied to the electrolysis  
10 apparatus at ambient pressure. Steam generators, though, generally provide steam at super-atmospheric pressures and the use of such higher pressures - typically up to 10 bar or even 100 bar - has the advantage of increasing efficiency.

15 The steam feed stream is generally supplied to the module via piping connected to the module so that the feed stream is passed across the surface of the substrate and undissociated steam together with oxygen produced are then carried away. At the cathode side, hydrogen gas produced is  
20 also generally exhausted by suitable piping. The piping (and conveniently also any external support such as a manifold or housing, for the substrate-supported membrane) may be made of any material known in the art but may conveniently be of steel or alumina, or the like.

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The steam feed stream is generally contacted with the substrate support, by passing a flow thereof across the exposed surface thereof.

30 Further preferred features and advantages of the present invention will appear from the following detailed

description given by way of example of some preferred  
embodiments described with reference to the accompanying  
drawings in which:

Fig.1 is a schematic section through a steam electrolyser  
5 module of the invention; and

Fig.2 is a schematic perspective view of a manifold  
interconnector for a multi-module electrolyser.

Fig.1 shows a steam electrolyser module 1 of the invention  
10 mounted in a manifold 2 and coupled to gas flow pipes 3,4 at  
cathode and anode sides 5,6 thereof, respectively. In more  
detail, the module 1 comprises a 5  $\mu$ m thick dense non-porous  
proton-conducting membrane 7 of BCY10 or BCN18 deposited on  
a 2 mm thick LSM substrate 8 having a 40% porosity and a  
15 pore size generally in the range of from 0.5 to 10  $\mu$ m.

On the outer face 9 of the membrane 7 (remote from the  
substrate support 8) is provided a porous metallic platinum  
cathode or hydrogen electrode 10, on top of which is  
20 provided a steel mesh current collector 11 connected 12 to  
the negative pole 13 of a DC voltage supply 14. At the  
anode side outer face 6 of the substrate 8 is provided a  
steel mesh current collector 15 connected 16 to the positive  
pole 17 of the DC voltage supply 14 so that a positive  
25 voltage is applied to a thin (30  $\mu$ m thick) layer 18 of the  
substrate 8 adjacent the membrane 7, which functions as an  
anode or steam electrode. The module 1 is electrically  
insulated from the steel manifold 2 and pipes 3,4 by a high  
temperature barium silicate glass ceramic seal 19.

The anode side pipe 4 has an inlet branch 4a through which high temperature steam 20 is fed in and passed across the exposed anode side outer face 6 of the substrate 8. Any undissociated steam 21, together with oxygen 22 produced by the electrolytic dissociation of the steam feed, are exhausted by an outlet branch 4b of the anode side pipe 4. The cathode side pipe 3 is used to exhaust hydrogen gas 23 liberated at the cathode 10.

10 In use of the above module the following processes occur:

at the anode  $2\text{H}_2\text{O} \rightarrow 4\text{H}^+ + \text{O}_2 + 4\text{e}^-$

at the cathode  $4\text{H}^+ + 2\text{e}^- \rightarrow 2\text{H}_2$

Fig. 2 shows part of a large scale steam electrolyser comprising a manifold interconnector 24 mounting multiple modules 1 such as those of Fig. 1.

#### Example 1 - Preparation of Proton Conducting Membrane Material

20 A nominal  $\text{BaZr}_{0.8}\text{Y}_{0.2}\text{O}_{2.9}$  powder was prepared by a solid state reaction method. For example, 9.8675g  $\text{BaCO}_3$ , 4.9288g  $\text{ZrO}_2$  and 1.1291g  $\text{Y}_2\text{O}_3$  powders were dried at 500-700°C before mixing together and ball-milling in a zirconia container with zirconia balls. The mixture was fired at 1400°C for 10  
25 hours.

The required amount of sintering aid was mixed together with as-fired powder, ball-milled for 15 minutes twice, then pressed into pellets having a diameter of 13mm, before  
30 firing at 1350°C. Pure ZnO was used as the sintering aid and a dense  $\text{BaZr}_{0.8}\text{Y}_{0.2}\text{O}_{2.9}$  pellet was obtained. To minimise the effect of addition of ZnO on the other properties such as

its conductivity, the amount of ZnO added was kept to a minimum. Less than 1wt% of ZnO, however, would require a higher temperature in order to effectively sinter the  $\text{BaZr}_{0.8}\text{Y}_{0.2}\text{O}_{2.9}$  pellets.

5

With the addition of only 1 w/w % ZnO,  $\text{BaZr}_{0.8}\text{Y}_{0.2}\text{O}_{2.9}$  pellets may be readily sintered at a temperature as low as 1350°C. A relative density of 96% was obtained after firing the  $\text{BaZr}_{0.8}\text{Y}_{0.2}\text{O}_{2.9}$  pellets at 1350°C for 10 hours with addition of 1wt% ZnO. For comparison, pellets pressed from 1400°C/10h  $\text{BaZr}_{0.8}\text{Y}_{0.2}\text{O}_{2.9}$  powder without any ZnO, were also fired at 1350°C for 10 hours together with the pellets with 1wt% ZnO sintering aid. The latter were found to have a much lower relative density of only around 68% and cracked into powders after exposure to air for just a few days.

Example 2 - Preparation of Membrane Material using direct solid state reaction to incorporate zinc into the lattice.

20  $\text{BaCe}_{0.5}\text{Zr}_{0.3}\text{Y}_{0.16}\text{Zn}_{0.04}\text{O}_{2.88}$  was prepared using 9.8675g  $\text{BaCO}_3$ , 4.3030g  $\text{CeO}_2$ , 1.8483g  $\text{ZrO}_2$ , 0.9032g  $\text{Y}_2\text{O}_3$  and 0.1627g ZnO, which were mixed together and ball-milled at high speed in zirconia container with zirconia balls for 15 minutes twice with addition of acetone. The mixture was dried to remove 25 the acetone, then pre-fired at 1100°C for 2 hours. The as-fired powders were pressed into pellets 13mm in diameter or fired at 1300°C for 10 hours. Dense pellets with relative density over 96% were obtained by this process. This Example shows that  $\text{BaCe}_{0.5}\text{Zr}_{0.3}\text{Y}_{0.16}\text{Zn}_{0.04}\text{O}_{3.8}$  was fully sintered at 1300°C 30 by introducing a small amount of zinc at the B-site and that

ZnO is an effective sintering aid for low temperature sintering of  $\text{BaCeO}_3$  and  $\text{BaCe}(\text{Zr})\text{O}_3$ -based perovskites.

#### Example 3 - Properties of Membrane Material

5 The conductivity of the material obtained in Example 2 was measured by ac impedance spectroscopy and the total conductivity found to compare favourably with previous data as shown in Figure 3. A pellet of the material (thickness 1.453 mm) was investigated in a concentration cell with  
10 platinum electrodes between hydrogen and oxygen passing through room temperature water. The open circuit potential using the above described membrane material decreased with increasing temperature as oxide transport started to compete with proton conduction as shown in Figure 4. This is  
15 expected behaviour for an intermediate temperature proton conductor.

Example 4 - Fabrication of a dense proton conducting thin film membrane on a porous substrate.

20 Porous  $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$  (LSM) substrates were prepared by tape casting. The liquid mixture used for tape casting consists of commercial submicron-size LSM powder (Praxair), graphite powder used as pore former, a (3:1) mixture of methyl ethyl ketone and ethanol as solvent, polyethylene glycol and di-n-  
25 butyl phthalate as dispersant and plasticizer, respectively and polyvinyl butyral resin binder (commercially available as Butvar®B-98). The mixture comprising powder, solvent (1:1 mixture to the powder) and pore former (40 wt%) was ball milled overnight on a roller ball mill using zirconia balls  
30 for breaking the agglomerates and reducing the particle size. The organic additives (dispersant, plasticizer and binder, also 40wt% referring to LSM) were then added and the

slurry was mixed in an electrical shaker for half an hour. The organic additives are meant to increase the viscosity of the slurry and to add strength and flexibility to the green tape. A subsequent ball milling for 4 hours is performed for  
5 homogenization of the slurry. The slurry was then used for green tape deposition using a tape casting machine and the resultant dried tapes were cut, overlapped and cut into 2.5 cm diameter disks. The disks were then fired with a slow ramp rate of 0.5°C to 1000°C for burning the organic  
10 residues, kept there for 5 hours and then fired to 1300°C for sintering and increasing the mechanical strength. The 2 cm diameter porous LSM disks presents around 50% porosity and a rather uniform distribution of micron size pores within the structure. In most of the cases, a thin layer of  
15  $\text{La}_{0.8}\text{Sr}_{0.2}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_{3-x}$  (LSCM) as a buffering layer was deposited by spray coating to prevent the reaction between the LSM substrate and  $\text{BaCe}_{0.5}\text{Zr}_{0.3}\text{Y}_{0.16}\text{Zn}_{0.04}\text{O}_{3-\delta}$  (BCZZY) electrolyte. The slurry used for spraying was prepared in a similar manner as above, increasing the amount of solvent used. The as  
20 prepared substrates are placed on a hot plate and held at about 300-350°C while about 10 ml of electrolyte suspension (2 g BCZZY ultrasonically dispersed in a mixture containing 35 ml ethanol) was sprayed onto the substrate using an airbrush. During deposition it must be ensured that the  
25 suspension hits the surface of the substrate while wet, allowing the remaining solvent to wick into the porous substrate before evaporation and avoiding solution pooling. The green bilayer is then sintered to 1325-1350°C for 5 hours using an alumina disk placed on top of the eletrolyte  
30 to ensure flatness of the assembly. The resulted structure was a porous LSM substrate deposited with a less porous,



very thin layer of LSCM and a dense film of BCZZY of approximately 10-40 microns thickness. An electron scanning micrograph of a cross section through a sample of the structure is shown in figure 5.

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Example 5 - Laboratory test of a steam electrolyser assembly with a BCZZY membrane

10 An LSM-BCZZY substrate-membrane assembly generally similar to that illustrated in Figure 1 was prepared by tape-casting (substrate) and spray-coating (membrane) as described in Example 4 above. The BCZZY-membrane was about 40  $\mu\text{m}$  thick and was provided with a porous Palladium Cathode. At the Anode there was provided a Platinum mesh Anode/current  
15 collector. The steam feed stream (to the Anode) used a pure oxygen supply as a carrier for the steam in order to avoid possible contamination of the cell components.

The steam partial pressure of the steam feed stream gas was  
20 controlled by bubbling the gas through a water bath that was kept at ambient temperature in this instance achieving a steam partial pressure of 0.022 bar and providing a gas composition of 2.2 vol%  $\text{H}_2\text{O}$  and 97.8 vol%  $\text{O}_2$ , to the Anode. A  
- gas mixture comprising hydrogen and argon was similarly  
25 bubbled through ambient water to supply a gas having a composition of 2.2 vol%  $\text{H}_2\text{O}$ , 5 vol%  $\text{H}_2$  and 92.8 vol% Ar to the cathode. Each of the gas flows was typically adjusted to 200 ml/cm<sup>3</sup>.

30 The amount of hydrogen produced was determined from the potential on a zirconia oxygen sensor using the Nernst

equation and the water dissociation equilibrium constant as detailed below in equations (1) and (2). The zirconia oxygen sensor was positioned in the exit gas flow and was kept at  $T = 766\text{ }^{\circ}\text{C}$ . At zero applied current and an electrolysis cell temperature of  $605\text{ }^{\circ}\text{C}$ , the gas partial pressures in the gas mixture were  $p_{\text{O}_2} = 1.125 \times 10^{-20}\text{ bar}$ ,  $p_{\text{H}_2\text{O}} = 0.0223\text{ bar}$  and  $p_{\text{H}_2} = 0.0496\text{ bar}$  (at  $766\text{ }^{\circ}\text{C}$ ). When a constant current of  $15\text{ mA}$  was applied to the electrolysis cell, the change in potential,  $E$ , of the cell is shown in Fig. 6. From the voltage output, EMF, of the zirconia sensor, and using equations (1) and (2) below, it was calculated that  $p_{\text{O}_2}$  decreased to  $9.840 \times 10^{-21}\text{ bar}$ , which corresponded to an increase of  $p_{\text{H}_2}$  to  $0.0531\text{ bar}$  and a conversion of ca. 16% of the steam that was contained in the gas mixture supplied to the anode, to hydrogen gas released at the cathode.

$$\text{EMF} = (RT/4F) \log_e (P_1(\text{O}_2) / P_2(\text{O}_2)) \quad (1)$$

$$K_f = p(\text{H}_2\text{O}) / (p(\text{H}_2) \cdot (p(\text{O}_2))^{1/2}) \quad (2)$$

20

wherein  $E$ ,  $R$ ,  $T$ , and  $F$  represent cell voltage, the Gas constant, temperature and the Faraday constant, respectively and  $K_f$  is the thermodynamic equilibrium constant for the dissociation of water to hydrogen and oxygen,  $\text{H}_2\text{O} \rightleftharpoons \text{H}_2 + \text{O}_2$ .

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# CLAIMS

1. A method of producing hydrogen comprising: providing a steam feed stream, contacting said steam feed stream with a proton conducting membrane supported on a porous redox  
5 stable substrate, through said substrate, said membrane being substantially non-permeable to molecular gas and to oxide ions, applying a DC voltage across an anode coupled to the substrate side of said membrane and a cathode coupled to the other side of said membrane so as to dissociate at least  
10 part of said steam feed stream therebetween, into protonic hydrogen and oxygen at said anode, allowing said protonic hydrogen to pass through said membrane and form molecular hydrogen at said cathode, and collecting said molecular hydrogen.

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2. A method as claimed in claim 1 wherein steam electrolysis is carried out at a temperature of from 400 to 800°C.

20 3. A steam electrolyser apparatus for producing hydrogen, comprising: a dense proton-conducting membrane substantially non-porous to molecular gas, said membrane being supported on a gas permeable, chemically and mechanically stable, electronically conducting substrate, said membrane being  
25 coupled: at the substrate - supported side to an anode for connection to a positive voltage, and to a steam inlet and oxygen outlet for feeding a steam feed stream into said substrate and exhausting oxygen gas released therefrom; and at its other side to a cathode for connection to a negative  
30 voltage and a hydrogen gas outlet for exhaustion of hydrogen gas released at said cathode.

4. An apparatus as claimed in claim 3 wherein the substrate material is electrochemically active and the anode constitutes part of the substrate adjoining the membrane.
- 5 5. An apparatus as claimed in claim 3 wherein the anode comprises a thin layer of a different material interposed between the membrane and the substrate support.
6. Apparatus as claimed in any one of claims 3 to 5  
10 wherein the proton conducting membrane is often oxygen deficient perovskite of formula  $ABO_{3-\delta}$  wherein A and B represent metallic elements occupying the A and B sites of the perovskite lattice structure and  $\delta$  represents the degree of oxygen deficiency.
- 15 7. Apparatus as claimed in claim 6 wherein said membrane material is selected from  $BaCe_{0.9}Y_{0.1}O_{2.95}$  (BCY10),  $BaZr_{0.9}Y_{0.1}O_{2.95}$  (BZY) and members of the solid solution,  $BaCe_{0.9-x}Zr_xY_{0.1}O_{2.95}$  (BCZY), or the analogues of the previously mentioned phases  
20 with lanthanides such as Gd, Nd or Yb instead of Y and such phases with higher degrees of substitution such as  $BaCe_{0.8}Y_{0.2}O_{2.95}$  (BCY20),  $Sr_3CaZr_{0.5}Ta_{1.5}O_{8.75}$  (SCZTO) and  $Ba_3Ca_{1.18}Nb_{1.82}O_{8.73}$  (BCN18) composites of such materials.
- 25 8. Apparatus as claimed in any one of claims 3 to 7 wherein the membrane is provided with an outer protective layer.
9. Apparatus as claimed in any one of claim 3 to 8 wherein  
30 the membrane thickness is not more than 25 $\mu$ m.

10. Apparatus as claimed in claim 9 wherein the membrane thickness is from 3 to 15 $\mu$ m.

11. Apparatus as claimed in any one of claims 3 to 10  
5 wherein the membrane comprises a BaZrO<sub>3</sub>-based material.

12. Apparatus as claimed in claim 11 wherein said BaZrO<sub>3</sub> based material is prepared with the use of a sintering aid.

10 13. Apparatus as claimed in claim 12 wherein the membrane is of BaZr<sub>1-x</sub>Ln<sub>x</sub>O<sub>3-x/2</sub> wherein X has a value in the range from (0.02) to (0.25) and Ln is a lanthanide ion or La, Y, Sc, and wherein said membrane is produced with the use of approximately 1% w/w of ZnO sintering aid.

15

14. Apparatus as claimed in any one of claims 3 to 13, wherein the substrate support is of a material which comprises a metallised ceramic or a mixed conductive oxide, having an electrical conductivity of not less than 10 S cm<sup>-1</sup> at  
20 the operating temperature of the steam electrolysis.

15. Apparatus as claimed in claim 14 wherein said substrate material is selected from Cu:Al<sub>s</sub>O<sub>3</sub>, La<sub>0.8</sub>Sr<sub>0.2</sub>MnO<sub>3</sub> (LSM), chromium-doped LSM (i.e. La<sub>0.75</sub>Sr<sub>0.25</sub>Cr<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>3</sub>) and  
25 La<sub>0.6</sub>Sr<sub>0.4</sub>Co<sub>0.2</sub>Fe<sub>0.8</sub>O<sub>3-d</sub> (LSCF).

16. Apparatus as claimed in any one of claims 3 to 15 wherein the substrate support pore size is not less than 0.5  $\mu$ m.

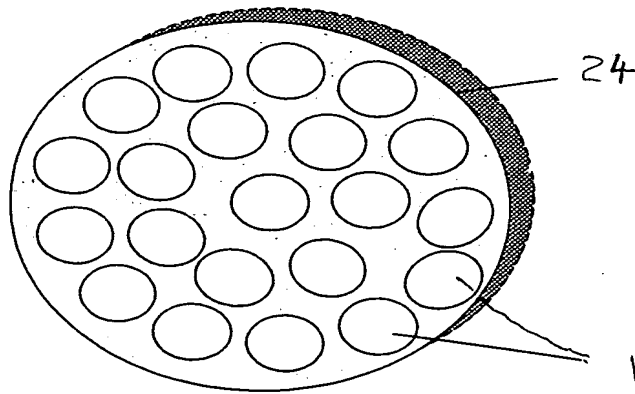
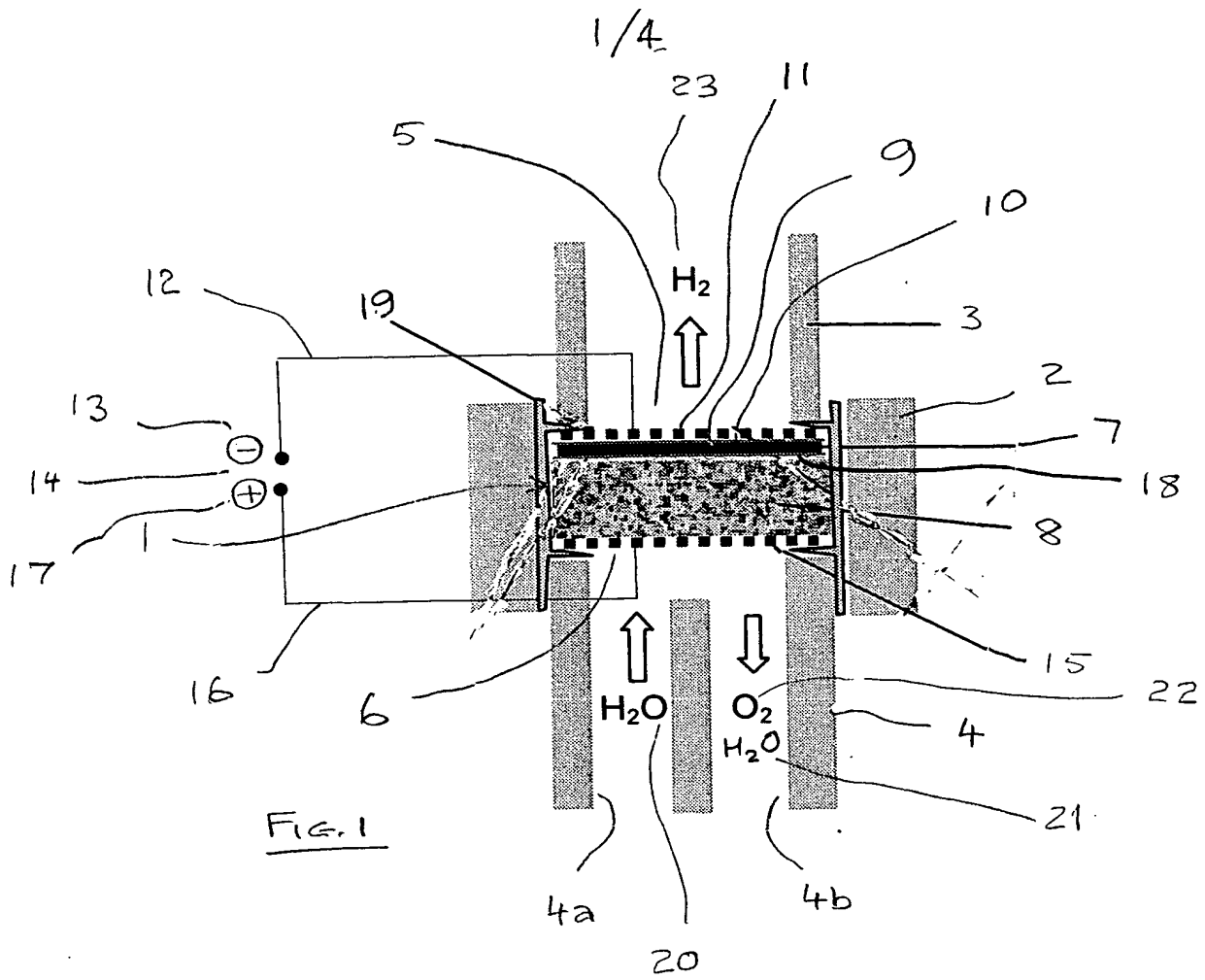
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17. Apparatus as claimed in any one of claims 3 to 16 wherein the substrate porosity is from 30 to 60%.

**ABSTRACT**  
**STEAM ELECTROLYSIS**

The present invention relates to a method of producing  
5 hydrogen comprising: contacting steam 20 with a proton  
conducting membrane 7 supported on a porous redox stable  
substrate 8, through said substrate 8. The membrane 7 is  
non-permeable to molecular gas and to oxide ions. A DC  
voltage is applied across an anode 15 coupled to the  
10 substrate side of the membrane and a cathode 9,11 coupled  
to its other side so as to dissociate at least part of the  
steam 20, into protonic hydrogen and oxygen at said anode  
15. The protonic hydrogen passes through the membrane and  
forms molecular hydrogen 23 at the cathode 9, 11.





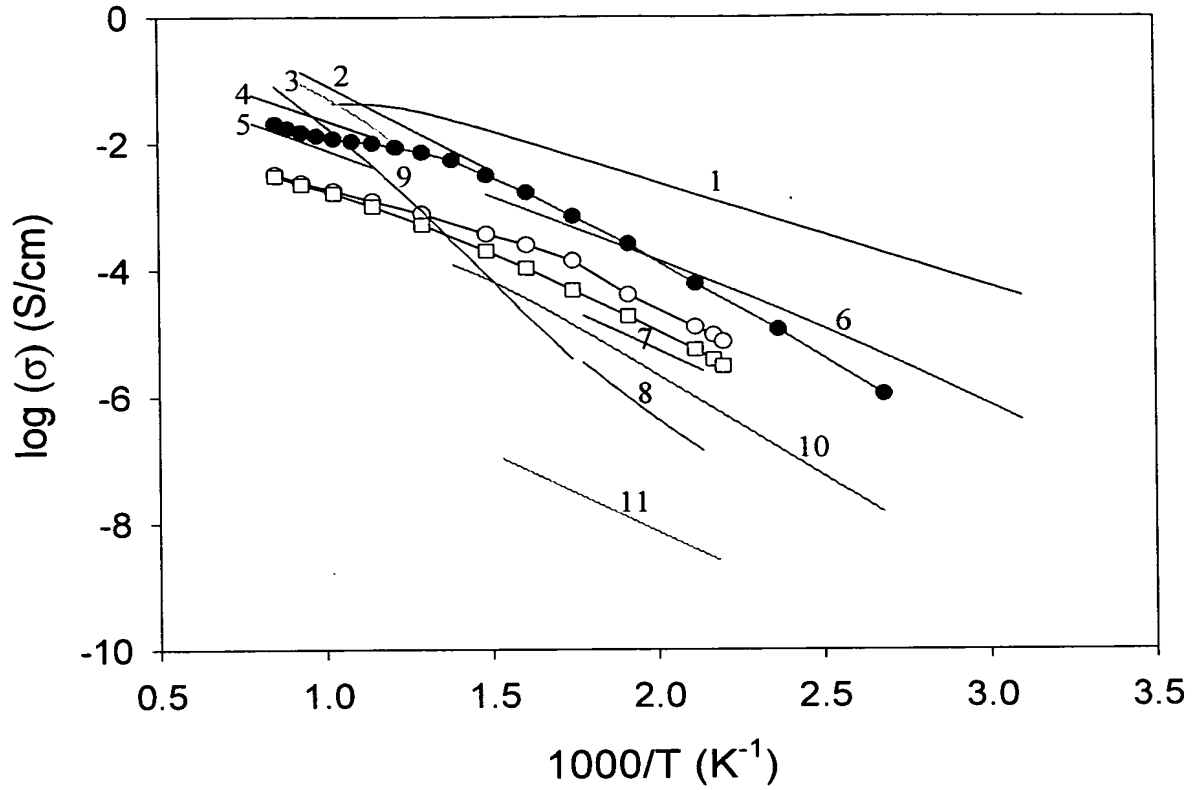


Fig. 3 - Comparison of conductivity of ionic conductors

Key: (1)  $\text{BaZr}_{0.8}\text{Y}_{0.2}\text{O}_{2.9}$  bulk (deduced) [1];

(2)  $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$  [2]; (3)  $\text{a}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{2.95}$  [3];

(4)  $\text{BaCe}_{0.9}\text{Y}_{0.1}\text{O}_{2.95}$  [4]; (5)  $\text{BaCe}_{0.5}\text{Zr}_{0.4}\text{Y}_{0.1}\text{O}_{2.95}$  [4];

(6)  $\text{BaZr}_{0.8}\text{Y}_{0.2}\text{O}_{2.9}$  total [5]; (7)  $\text{BaZr}_{0.9}\text{Y}_{0.1}\text{O}_{2.95}$  bulk [6];

(8)  $\text{BaZr}_{0.9}\text{Y}_{0.1}\text{O}_{2.95}$  total [6]; (9)  $\text{Y}_{0.15}\text{Zr}_{0.85}\text{O}_{2.8}$  (YSZ) [2];

(10)  $\text{BaCe}_{0.7}\text{Zr}_{0.2}\text{Nd}_{0.1}\text{O}_{3.8}$  [7]; (11)  $\text{BaZr}_{0.8}\text{Y}_{0.2}\text{O}_{2.9}$  film total [8];

O  $\text{Ba}_{0.97}\text{Zr}_{0.77}\text{Y}_{0.19}\text{Zn}_{0.04}\text{O}_{3.8}$  bulk in wet 5%  $\text{H}_2$ ;

□  $\text{Ba}_{0.97}\text{Zr}_{0.77}\text{Y}_{0.19}\text{Zn}_{0.04}\text{O}_{3.8}$  total in wet 5%  $\text{H}_2$ ;

●  $\text{BaCe}_{0.5}\text{Zr}_{0.3}\text{Y}_{0.16}\text{Zn}_{0.04}\text{O}_{3.8}$  total in wet 5%  $\text{H}_2$ .

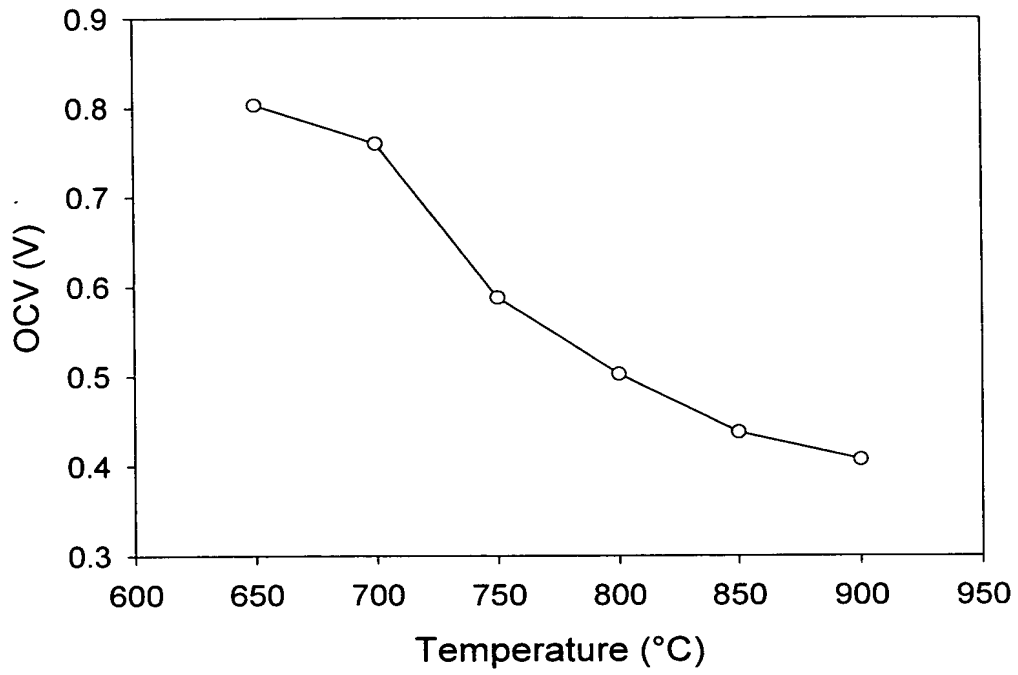


Fig. 4 - Open circuit voltage (OCV) of BCZZY cell

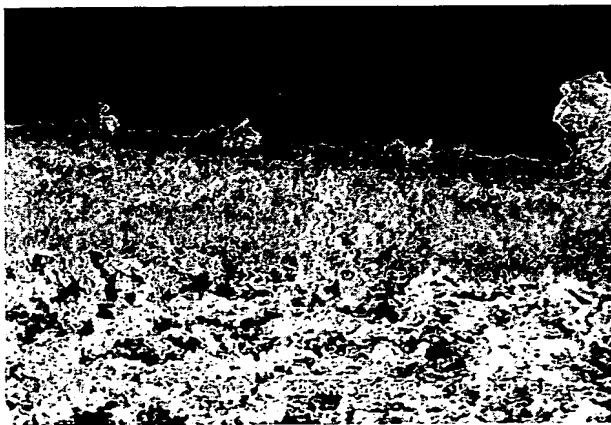
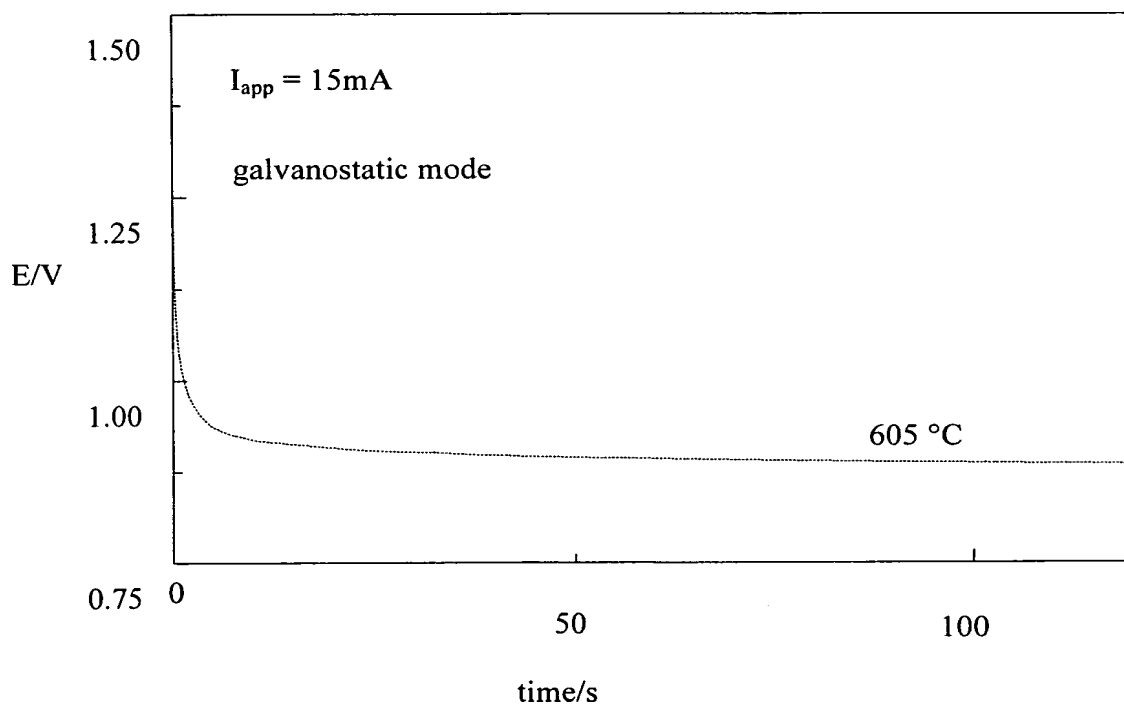


Fig. 5 - Membrane cross-section

Fig. 6 - Measurement of Change in Gas Composition



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